



Why Boiler O&M engineers should know boiler water chemistry?

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Can we prevent boiler tube corrosion by controlling boiler water chemistry alone? In this article I will be pondering this question from a Boiler O&M engineer's perspective.

Honestly speaking, I do not have a vast knowledge on Chemistry. In fact, most of the engineering professionals working in boiler O&M I have known are not exactly enthusiastic about chemistry, I dare say. They feel it is best be dealt by those, who are having a pure chemistry background.

But then, water chemistry in boiler is not just pure chemistry, isn't it? If it was, then why would one consider the pH value of 8 in the boiler water as highly acidic?

Let us first take the case of acidic corrosion and caustic corrosion in the water wall. Acidic corrosion occurs in the pH region of 4 to 5 and caustic corrosion in the pH region of 12.5+. But in most of the sub-critical boiler system (with steam drum), we are maintaining the drum pH in the range of 9.4 to 9.5. Even in the small process boilers, where the drum pH is kept higher, we rarely exceed 10.5. So we should not face these problems, but then, we do face these problems. Recently I have dealt with severe corrosion issues in the CPP boilers at two different Refinery plants.

Yes, water chemistry was an issue in both cases, but it was not the only issue!

First let us take a look at where they have happened. Sample 1 & 2 have taken place on the rear water wall tubes from CPP boiler of one plant, where as sample 3 is from roof tube of another refinery CPP boiler.



Sample 1



Sample 2



Sample 3

In sample 1 & 2, indication of caustic corrosion mechanism was confirmed. The XRD analysis of the deposit collected from the failure samples reveals presence of NaOH and NaFeO₂ that results from caustic gouging corrosion. Whereas in case 3 that belongs to another refinery CPP boiler, the acidic corrosion mechanism was confirmed. EDS analysis (XRD analysis couldn't be carried out in this case) of the deposit collected from this sample indicated Chlorine along with Calcium and Magnesium and the pH of the solution prepared with the deposit was less than 6.

What was common in both cases are the parallel marks that can be seen along the tube length at 12 'O' clock position (fire side) along which corrosion took place.



These are clear indication of corrosion taking place below steam stratification (film boiling) on the water wall tube surface facing the fire.

Now let me bold enough to discuss the chemistry behind these two corrosion mechanisms.

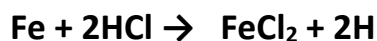
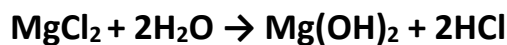
Caustic gouging corrosion:



The first reaction takes place in the evaporator when we doze TSP. Resultant NaOH (Caustic) increases the OH alkalinity and pH of the water and gives a residual phosphate in the system. But when there is **free caustic present** in the water, it first attacks the magnetite layer (second reaction) and then it gouges out the metal (third reaction).

But free caustic can be present in water when the pH is in excess of 12.5 but not if the pH is in the range of 9.4 – 9.5!

Acid Chloride corrosion:



The first reaction takes place in the boiler water when there is a chloride infiltration to the boiler water due to condenser leakage. While resultant Mg(OH)₂ is mildly basic, HCl is more acidic, resulting a little depletion of pH in drum. But if the pH goes down below 5.5, the HCl attacks the magnetite (second reaction), removes it and then attacks the metal. But it would not when the boiler water pH is maintained at 9.4 – 9.5, as we generally do!

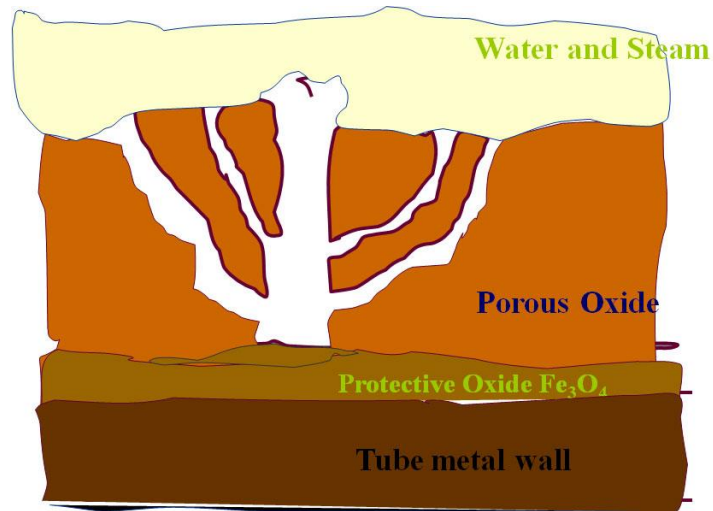
Local concentration increasing mechanism:

It can happen below a porous deposit (also called Wick Boiling), or below a layer of steam that may form over the surface of the tube (also called Film Boiling, or steam blanketing) after a Departure from Nucleate Boiling (DNB) takes place in the water wall tube.

These porous deposits are mostly corrosion product of iron carried in from the feed water system, often forming a deposit on the tube surface facing the fire.

If these deposits contain copper, or, zinc (resulting from corrosion of admiralty brass, a metallurgy often used for condenser tubes till a decade back), they significantly assist galvanic corrosion.

Below these porous deposits, boiler water seeps through the micro pours and gradually gets evaporated after receiving the heat from the tube wall.



Wick Boiling

As the solvent is lost, the concentration of dissolved impurities in this water increases many folds.

The pH could go either very high, or, very low, depending upon the dissolved impurities in it. It may lead to caustic corrosion if the pH is very high and acidic corrosion if the pH becomes very low.

Now the similar phenomenon will occur below a steam blanketing. Below the steam film, the concentration of contaminations would severely increase.

In both the cases referred earlier, clear indication of steam blanketing could be seen. While deposits could be controlled by maintaining proper feed water chemistry, in the film boiling, chemistry has absolutely no role to play. Every O&M engineering professional would know the factors leading to DNB and film boiling in a sub-critical boiler, which are improper circulation, or concentration of heat flux on the tube due to flame impingement or shifting. Not exactly a water chemistry issue, isn't it?

Take the case of oxygen pitting corrosion in the economizer outlet. Yes, dissolved oxygen concentration along with lower feed water pH are primarily responsible. But why it occurs mostly near the welding joints, or rather in the HAZ part of the welding joint?

Oxygen pitting corrosion is galvanic corrosion that occurs at a location where galvanic cell is formed. The strongest galvanic cell is formed at a location of conductive deposits of copper, zinc and iron. But it also forms at a location of differential stress!

In coal fired boilers, a number of economizer tubes are needed to be replaced due to thickness loss by ash erosion. During annual over hauling hundreds of welding joints are carried out and economizer welding joints are never required to be stress relieved. While DPT and RT ensures the quality of welding (basically ensures that there is no weld discontinuities), what check is there to ensure that there is no residual stress added during the welding process? When you have a large number of welding joints that needed to be completed within a deadline, you tend to carry them out quickly. The welding speed becomes higher and the electrode size becomes bigger. The welder uses higher current that results in to more heat input, which leads to higher residual stress! Is water chemistry alone responsible here? Answer is No! Let us say the welder, or more correctly, the welding supervisor is responsible.

When the welding joint fittings are done in a hurry (Deadline...remember?), the fitting may have problems like mismatch. Now, if you are good welder, you can manage to fuse the joint properly, so that the radiography would not show any lack of fusion (a repairable defect). Only he would be using higher current to achieve that! So now who is responsible? The welder, or the fitter, or the faulty water chemistry alone?

The point I wanted to drive home is that it is really important to control the water chemistry, but there are many other factors in play which cannot be controlled by a chemist alone.

Therefore, every Boiler O&M engineering personnel should have the understanding of Boiler Water Chemistry!